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M. Thoss

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# Simulation of Electron Transfer and Electron Transport in Molecular Systems at Surfaces

**Pedro B. Coto, Chriszandro Hofmeister, Veronika Prucker,  
Dominik Weckbecker, and Michael Thoss**

Institut für Theoretische Physik and Interdisziplinäres Zentrum für Molekulare Materialien,  
Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7/B2, 91058 Erlangen, Germany  
*E-mail: michael.thoss@physik.uni-erlangen.de*

We have investigated electron transfer and transport processes in several molecular systems adsorbed at metal surfaces using a methodology that combines first-principles electronic structure methods with quantum dynamics and transport approaches. Specifically, we have analysed the molecular factors that control electron transfer in a series of nitrile-substituted alkanethiolate self-assembled monolayer models adsorbed at the Au(111) surface that differ in the size of the aliphatic spacer chain. In addition, we have analysed the possibility of using a proton transfer reaction triggered by an external electrostatic field as a novel mechanism for switching a molecular junction. To demonstrate the feasibility of the process, we have investigated electron transport in a junction containing a molecular bridge that can exist in two tautomeric forms, [2,5-(4-hydroxypyridine)] and 2,5-[4(1H)-pyridone], that exhibit very different conductance properties.

## 1 Introduction

The transfer or transport of electrons is a key step in many processes in physics, chemistry, biology, and technology<sup>1</sup>. Examples range from intramolecular charge transfer in donor-acceptor complexes in solution<sup>2</sup> over ET in sensory proteins or photosynthesis<sup>3</sup> to charge transport processes in single-molecule junctions<sup>4</sup>. From the point of view of the design of nanoelectronic devices or new materials with improved characteristics, understanding the fundamental mechanisms of ET at the molecular level is all important. In this respect, theory and simulation can assist the interpretation of experimental results and provide additional information on the underlying ET mechanisms that is not straightforwardly obtained from experiment.

In the following, we discuss the theoretical methods employed and the results obtained in the simulation of ET processes involving organic molecules adsorbed at metal surfaces. Specifically, we report the results obtained in the investigation of the mechanism of ET in a series of nitrile-substituted alkanethiolate self-assembled monolayer (SAM) models adsorbed at the Au(111) surface that have aliphatic spacer chains of different size. In addition, we detail the results obtained in the characterisation of the transport properties of a single molecule junction with an organic molecular bridge that can exist in two tautomeric forms, [2,5-(4-hydroxypyridine)] and 2,5-[4(1H)-pyridone], characterised by very different conductance properties and discuss the possibility of using this device as a molecular switch.

## 2 Electron Transfer in Molecular Systems Adsorbed at Surfaces

In this section, we outline the results obtained in the theoretical investigation of the mechanism of electron transfer (ET) in molecular systems adsorbed at metal surfaces. We begin by a concise description of the theoretical methods employed and continue with the discussion of the results obtained in the simulation of the electron injection dynamics in a series of nitrile-substituted alkanethiolate SAM models adsorbed at the Au(111) surface.

### 2.1 Theoretical Methods

In the investigation of the dynamics of heterogeneous ET processes at metal surfaces we used a theoretical methodology that combines first principles electronic structure methods with quantum dynamical approaches.

The first step of this methodology is the characterisation of the most stable adsorption structure of the molecule at the surface. In this respect, the systems investigated in this work were modelled employing density functional theory (DFT) calculations with periodic boundary conditions in the low coverage limit using a slab model approach for the description of the molecule-surface system. These computations strongly benefit from the use of massive parallel computing environments like those provided by Jülich Supercomputing Centre. Specifically, the periodic DFT calculations were carried out employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional<sup>5</sup>, and the projected augmented wave method<sup>6</sup> using VASP<sup>7</sup>. For the systems investigated, accurate k-point meshes ( $10 \times 10 \times 1$ ) and energy cut-off (415.0 eV) for the plane wave basis sets were used<sup>8,9</sup>.

In the second step, the thus obtained optimised geometries were used to build cluster models of the different systems investigated. The size of the clusters was selected to minimise the artifacts that boundary effects may have in the simulation of the dynamics of the electron injection process. Specifically, we used slab and cluster models featuring five layers of Au atoms (comprising a total of 125 atoms) and the respective adsorbed molecules. The electronic structure calculations for the cluster models were performed using TURBOMOLE<sup>10</sup> at the DFT level of theory employing the PBE functional and the def-SV(P) basis set<sup>11</sup>. The core electrons of the Au atoms were described using an ECP<sup>12</sup>. We use the Kohn-Sham matrix to build the ET model Hamiltonian and obtain the donor and acceptor states, their energies, and the donor-acceptor coupling terms employing a method that is based on the projector operator approach to resonant electron-molecule scattering<sup>13,14</sup>. In this method, the ET model Hamiltonian is built according to the following procedure. First, the Hilbert space associated to the problem is partitioned into donor (organic molecule) and acceptor (Au(111) surface) subspaces using a localised basis. Second, the Hamiltonian is partitioned accordingly. Third, a separate diagonalisation of the donor and acceptor blocks of the Hamiltonian is carried out. The ET model Hamiltonian  $H$  obtained reads

$$H = \left( \begin{array}{ccc|ccc} E_{d,1} & 0 & \cdots & & & \\ 0 & E_{d,2} & \cdots & & & \\ \vdots & \vdots & \ddots & & & \\ \hline & & & E_{a,1} & 0 & \cdots \\ & & & 0 & E_{a,2} & \cdots \\ & & & \vdots & \vdots & \ddots \end{array} \right), \quad (1)$$

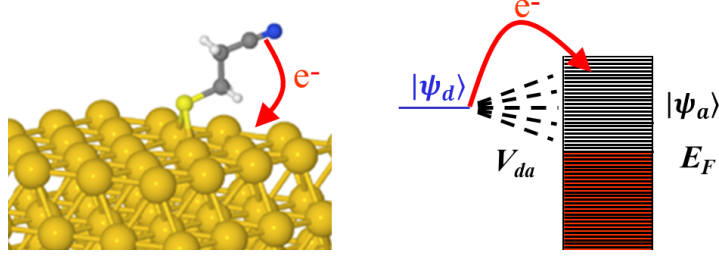


Figure 1. Schematic representation of the ET process. Left: Prototypical system investigated in this work consisting of an organic nitrile-substituted alkanethiolate molecule adsorbed at the Au(111) surface. Right: Energy level diagram for the ET process. The donor state,  $|\psi_d\rangle$ , is coupled to a quasi-continuum set of empty acceptor states,  $|\psi_a\rangle$ , through  $V_{da}$ , the donor-acceptor electronic coupling terms.  $E_F$  is the Fermi energy of the system.

where the diagonal blocks of  $H$  contain the energies of the  $i$  ( $E_{d,i}$ ) and  $j$  ( $E_{a,j}$ ) states of the donor and acceptor moieties, respectively. The eigenvectors of these blocks are identified with the localised states of the donor ( $|\psi_d\rangle$ ) and acceptor ( $|\psi_a\rangle$ ) fragments and the matrix elements of the off-diagonal blocks,  $V_{da}$ , are identified with the donor-acceptor electronic coupling terms. To incorporate the effects of the extended nature of the Au surface in the model ET Hamiltonian, we used a model inspired by the surface Greens function approach<sup>15</sup>. In this model, the self-energy (which accounts for the effects of the part of the infinite surface not included in the cluster models) is approximated by a complex absorbing potential (CAP)<sup>16</sup> that is added to  $H$  and that has the form

$$V_{\text{CAP}}(R) = \begin{cases} -i\alpha(R - 5)^\delta & \text{if } R > 5 \text{ bohr} \\ 0 & \text{if } R \leq 5 \text{ bohr} \end{cases} \quad (2)$$

where  $R$  is the distance between the considered Au atom and the sulphur atom of the nitrile-substituted alkanethiolate moiety (see Fig. 1) and  $\alpha$  and  $\delta$  are constants with values  $1.0 \times 10^7$  hartree/bohr<sup>4</sup> and 4, respectively, that were obtained after testing.

The aforementioned theoretical protocol provides the necessary information to obtain the time evolution of the population of the donor state,  $P_d(t)$  given by

$$P_d(t) = |\langle \psi_d | e^{-i\hat{H}t} | \psi_d \rangle|^2, \quad (3)$$

which we have used for the characterisation of the electron injection dynamics.

## 2.2 Application to Electron Transfer at Molecule-Metal Interfaces

The methodology detailed above has been applied to investigate the electron injection dynamics in a series of nitrile-substituted alkanethiolate SAM models (**C2**, **C3**, **C4**, and **C8**) having aliphatic spacer chains with an increasing number of methylene bridge groups ( $-(\text{CH}_2)_2-$ ,  $-(\text{CH}_2)_3-$ ,  $-(\text{CH}_2)_4-$ , and  $-(\text{CH}_2)_8-$ , respectively). We investigated the ET dynamics of the donor states  $\pi_1^*$  and  $\pi_2^*$  (see Fig. 2) corresponding to the two  $\pi^*$  resonances of the CN group whose electron injection dynamics has been studied using core-clock hole spectroscopy<sup>17,18</sup>. The motivation underlying the selection of these systems was twofold. On the one hand, they provide a way to investigate the role that the symmetry of the donor state has in the ET process. On the other hand, the use of systems with

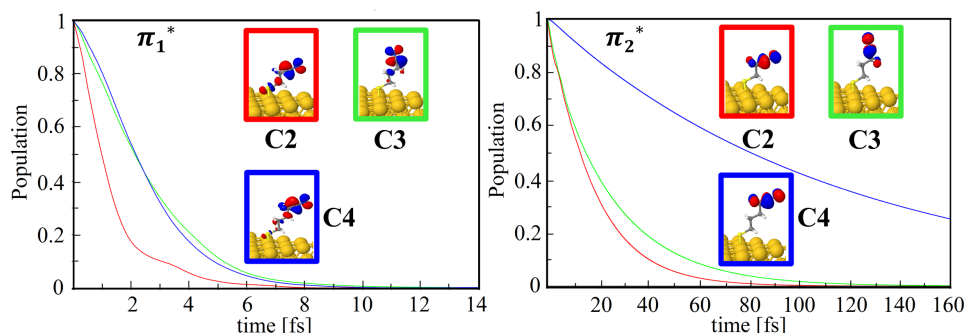


Figure 2. Population decay of  $\pi_1^*$  (left) and  $\pi_2^*$  (right) donor states for the nitrile-substituted alkanethiolate SAM models **C2** (red), **C3** (green), and **C4** (blue). The insets show the localised donor states  $|\psi_d\rangle$ .

aliphatic linkers of different size provides information about the roles that their electronic and chemical structures have in the ET mechanism.

The results obtained show that for all systems investigated, the most stable adsorption geometry was the bridge-fcc like position with the adsorbed molecule tilted against the surface normal with values ranging from  $68.8^\circ$  in **C4**, over  $70.7^\circ$  in **C2**, to  $73.6^\circ$  in **C8**. For **C3**, the only system having an odd number of methylene bridge groups, the tilting angle obtained was  $10.3^\circ$  (see Fig. 2). Regarding the electron injection dynamics, for all systems investigated the donor states  $\pi_1^*$  and  $\pi_2^*$  exhibit different ET times. In particular, electron injection times from the  $\pi_1^*$  donor state of **C2**, **C3**, and **C4** were found to be ultrafast, with characteristic times of  $\tau_{1/2} = 1.0$  fs,  $\tau_{1/2} = 2.1$  fs, and  $\tau_{1/2} = 2.2$  fs, respectively. On the other hand, the electron injection times from the  $\pi_2^*$  donor state were found to be systematically slower [ $\tau_{1/2} = 12.3$  fs (**C2**),  $\tau_{1/2} = 15.1$  fs (**C3**), and  $\tau_{1/2} = 80.5$  fs (**C4**)]. For **C8**, the electron injection time scales obtained are too long to be correctly described with the CAP method employed in the simulations. The results obtained can be rationalised on the basis of the symmetry of the donor state and the molecular structure of the spacers. Specifically, in all systems investigated the  $\pi_1^*$  donor states are more delocalised than the corresponding  $\pi_2^*$  donor states (see Fig. 2). This leads to larger molecule-substrate coupling  $V_{da}$  and therefore, faster electron injection dynamics, a result in qualitative agreement with the experimental data<sup>8</sup>. On the other hand, there is a systematic slowdown of the ET process with the increase in size of the aliphatic spacer chain in all systems investigated for both donor states. The reason for this behaviour is the increase of the distance between the donor and acceptor moieties, which leads to a decrease in the magnitude of  $V_{da}$ <sup>19</sup> and therefore to slower electron injection dynamics.

### 3 Electron Transport in Single Molecule Junctions

In this section, we discuss the results obtained in the simulation of ET in single molecule junctions. After a brief outline of the theoretical methods employed in the simulation of electron transport in molecular junctions, we report the results obtained in the characterisation of the transport properties of a junction with an organic molecular bridge that can exist in two tautomeric forms, [2,5-(4-hydroxypyridine)] and 2,5-[4(1H)-pyridone], and the possibility of using this device as a molecular switch.

### 3.1 Theoretical Methods

In the simulation of electron transport in single molecule junctions we have used the model Hamiltonian

$$H = \begin{pmatrix} H_L & H_{LM} & 0 \\ H_{ML} & H_M & H_{MR} \\ 0 & H_{RM} & H_R \end{pmatrix}, \quad (4)$$

that describes a single molecule junction consisting of a molecular bridge (M) and two leads (L and R) where the bridge is coupled to both leads and no direct coupling between the latter exists ( $H_{RL} = H_{LR} = 0$ ). The parameters needed for the construction of this model Hamiltonian have been obtained employing a partitioning technique similar to that described in Sec. 2.1. Specifically, the overall system was divided into two parts. The molecule and part of the leads were described explicitly using first-principles electronic structure methods. For the systems investigated, we used DFT employing the B3LYP hybrid exchange-correlation functional<sup>20–22</sup>, and a SV(P) basis set<sup>11</sup> (88 Au atoms were described using the ECP-60-MWB pseudopotential<sup>12</sup>). The remaining part of the leads was described using self-energies<sup>15</sup>. After adding the corresponding self-energies to the left and right leads the current-voltage characteristic can be obtained using the Landauer formula<sup>23</sup>

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E) [f_L(E) - f_R(E)] dE \quad (5)$$

where  $f_L(E)$  and  $f_R(E)$  are the Fermi distributions of the left and right leads, respectively, and  $T(E)$  is the transmission function that can be expressed as<sup>24</sup>

$$T(E) = \text{tr}_M [\Gamma_L(E) G_M^\dagger(E) \Gamma_R(E) G_M(E)] \quad (6)$$

where  $G_M(E)$  is the molecular Green's function,  $\Gamma_{L/R}(E)$  the broadening of the molecular states that results from the coupling to the continuum of states of the Au leads, and the trace is taken over the electronic states of the molecule (M)<sup>25</sup>.

### 3.2 Switching the Conductance of a Molecular Junction using a Proton Transfer Reaction

A single molecule junction may be used as a nanoswitch if the molecular bridge has at least two stable states with different conductance that can be reversibly transformed into each other by means of a mechanism that can be externally controlled. We have analysed the possibility of using a proton transfer reaction triggered by an external electrostatic field as a novel mechanism for switching a molecular junction. As an example, we have investigated this possibility using single molecule junctions containing tris{2,5-[4(1H)-pyridone]} (T2PY) and tris[2,5-(4-hydroxypyridine)] (T2HP) as bridges (see Fig. 3). Both tautomers were functionalised for binding to the Au leads with 3,4-dimercapto-(1H)-pyridine and 3,4-dimercaptobenzenone, and 3,4-dimercaptopyridine and 3,4-dimercaptophenol, respectively. To demonstrate the feasibility of the process we have investigated the transport properties of these junctions. Fig. 3 depicts the current-voltage characteristics of T2PY and T2HP. The results show that T2PY exhibits a rather low current for the range of  $V$  investigated whereas T2HP exhibits larger current, in particular for bias voltages  $|V| > 0.5$  V. This different behaviour originates from the differences in

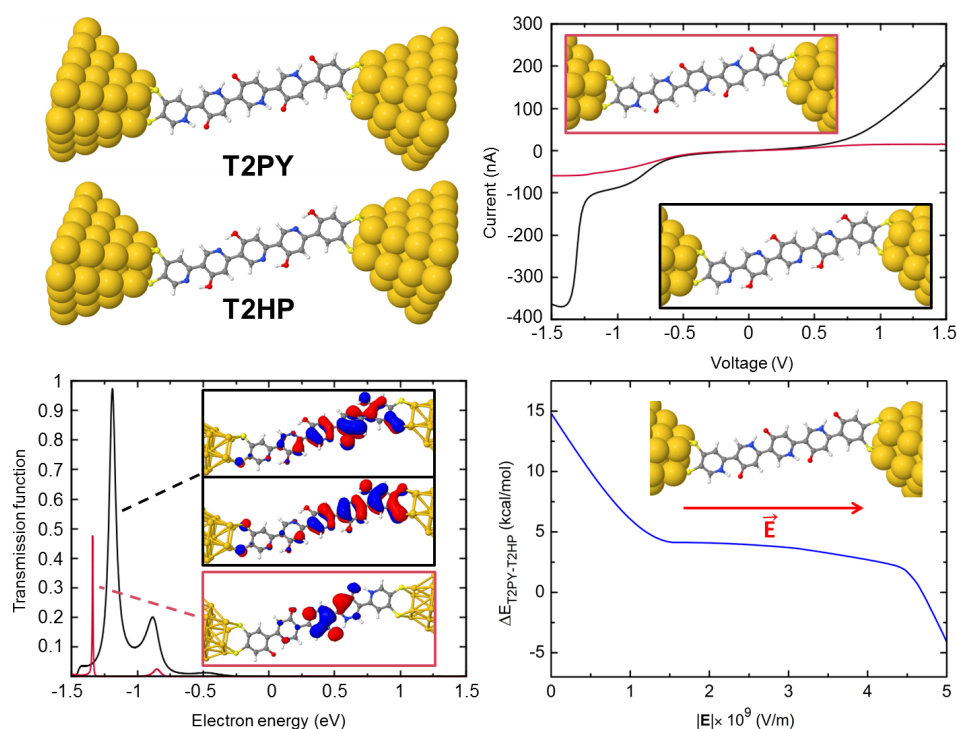


Figure 3. Top, left: Molecular junctions investigated in this work. Right: Current-voltage characteristics. The black and red lines correspond to T2HP and T2PY, respectively. Bottom, left: Transmission function for T2HP (black) and T2PY (red). The molecular orbitals associated to the most significant peaks of  $T(E)$  are also shown. Right: Energy difference between T2PY and T2HP for different values of the applied external electrostatic field. The inset shows the direction of the field<sup>26</sup>.

the electronic structures of both tautomers, specifically the degree of delocalisation of the  $\pi$  bond network<sup>26</sup>. As shown in Fig. 3, the molecular orbitals associated with the most relevant structure of the transmission function of T2HP, the peak at  $E = 1.25$  eV, are  $\pi$ -like orbitals that extend over the molecule while in the case of T2PY the most relevant feature, the peak at  $E = -1.4$  eV, is associated with a  $\pi$ -like orbital that has most of its density localised in the centre of the molecule. Therefore, for a given bias voltage the two tautomers show different conductance and can be associated with the “on” (T2HP) and “off” (T2PY) states of a molecular switch. The second condition necessary a functional switch is the existence of a mechanism for the reversible transformation between the stable minima. In the case investigated the tautomers can be interconverted via a proton transfer. To explore this possibility, we have studied the relative stability of both T2HP and T2PY in the presence of a constant external electrostatic field oriented in a direction along the axis of the junction (see Fig. 3). The results obtained show that it is possible to obtain an inversion of the relative stabilities of T2HP and T2PY by increasing the strength of the external electrostatic field applied, therefore providing a proof of principle that a reversible interconversion between T2HP and T2PY using this mechanism is possible.

## 4 Concluding Remarks

We have described a theoretical methodology for the investigation of electron transfer and transport processes in molecular systems adsorbed at surfaces that combines first-principles electronic structure methods with quantum dynamics and electron transfer approaches. Using this methodology we have investigated the factors controlling the electron injection dynamics in a series of nitrile-substituted alkanethiolate SAM models adsorbed at the Au(111) surface. In addition, we have explored the possibility of using a proton transfer reaction triggered by an external electrostatic field as a novel mechanism for switching a molecular junction, providing a proof of principle of the feasibility of the process. The results obtained may pave the way for the design of new nanoelectronic devices.

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